



Studies on obtaining of aluminium phosphates modified with ammonium, calcium and molybdenum



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ARTICLE INFO

Article history:

Received 1 July 2014

Received in revised form 1 August 2014

Accepted 20 August 2014

Available online 27 August 2014

Keywords:

Conventional reaction
Anticorrosive pigments
Aluminium phosphate
Modified phosphates

ABSTRACT

Studies on obtaining of aluminium phosphates modified with ammonium, calcium and molybdenum were implemented. Reagent grade substrates $(\text{NH}_4)_2\text{HPO}_4$, CaCO_3 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, aqueous ammonia, and amorphous $\text{Al}(\text{OH})_3$ were prepared and used in the experiments. An influence of process parameters, i.e. reaction time (60 ± 30 min) and total salt concentration (50 ± 10 wt%) on the phase composition and product properties was determined. Statistical software STATISTICA 10 for planning and evaluation of the experiments was used. Based on the statistical evaluation of planned research by the plan fractional factorial design at three levels $3^{(k-p)}$, process parameters allowing to obtain the material of with expected physicochemical properties were determined. The content of aluminium, calcium and molybdenum in the products was determined using ICP-AES technique. The phosphates and ammonium content was determined by means of a spectrophotometric method and ion selective electrode Orion 11–35 type, respectively. The phase composition of the obtained materials was studied using XRD analysis. The specific surface area was calculated using the BET method and the particle size was determined by LSM. The Tafel experiments for an uncoated mild steel (immersed in an aqueous phosphate extract in 3.5 wt% NaCl solution) were performed. The steel corrosion products as well as tested phosphates were examined by means of scanning electron microscope with a cold field emission coupled with the energy dispersive X-ray analyzer. The content of the individual components was in the range of 10.52–16.33 wt% (Al), 10.59–18.54 wt% (Ca), 0.59–5.28 wt% (Mo), 0.1–4.91 wt% (NH_3), and 6.97–23.4 wt% (P_2O_5). The products were characterized by different physicochemical parameters. The surface area was in the range from 6 to 63 m^2/g and the oil absorption was 36–71 g of oil/100 g of product, whereas the average particle size of products reached 221–319 nm. The Tafel tests revealed markedly higher anticorrosive properties of aluminium phosphates modified with ammonium, calcium, molybdenum in comparison to commercial aluminium phosphate and zinc phosphate.

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Introduction

The most widespread protection method of metallic materials is covering with anticorrosive paints based on organic binder. The efficacy of that method depends on chemical or electrochemical reactions of an anticorrosive pigment with a metallic substrate in presence of corrosive medium penetrating throughout the layer of organic coating [1]. Several approaches have been proposed in recent years to produce the coatings revealing enhanced anticorrosive properties. One of the efficient ways to improve the

protective performance of organic coatings is to incorporate inorganic anticorrosive pigments belonging to the electrochemically active class [2–6]. As a distinguished representative of electrochemically active class, chromate-based pigments have been reported however, due to increasing concerns for environmental and human health protection their usage has been heavily restricted [7–11]. The increasing pigments consumption, the desire for a new interesting color pigment, and the fact that many pigments contain toxic elements (e.g. Pb, Cr, Sb, Cd, Se), has opened the door to the development of novel environmentally friendly powder products [12,13]. Different kinds of anticorrosive pigments have been utilized in order to enhance the protective properties of organic coatings. Size, shape, surface modification and chemical composition of pigments are important parameters affecting theirs

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corrosion inhibition activity. Using of inorganic pigments with capability of releasing corrosion inhibiting species is an important way to achieve a reliable and long-lasting corrosion protection performance [14]. Environmental protection issues restrict the use of toxic pigments, hence a new generation of pigments, such as phosphates of zinc, molybdenum, calcium, and aluminium, has been developed and widely used as anticorrosive pigments. However, the environmental regulations dealing with heavy metals are becoming stringent and development of a more efficient and environmentally friendly pigment is required [15–17].

Although aluminium phosphate modified with calcium or ammonium [22] as well as synthetic fillers based on various compounds of molybdenum (basic zinc molybdate, basic calcium zinc molybdate, phosphomolybdates) [23] have been successfully applied in protective coating compositions for a steel substrate, corrosion inhibition properties of aluminium phosphates containing ammonium, calcium and molybdenum have not been described in a literature. The aim of the presented work was to elaborate the preparation process of aluminium phosphates modified with ammonium, calcium and molybdenum as well as to investigate their steel corrosion inhibition efficiency by means of potentiodynamic polarization technique. An influence of preparation process parameters on several physicochemical properties of the products such as chemical composition, oil absorption and specific surface area were determined. Based on the Tafel test results the corrosion potential, corrosion current density and corrosion rate for steel immersed in phosphate extract in an aqueous NaCl solution were calculated and presented.

Experimental

Procedure

Studies on the synthesis of aluminium phosphates modified with ammonium, calcium and molybdenum were performed on the basis of the experimental planning and analysis according to a three-level $3^{(k-p)}$ fractional factorial designs with 9 experiments with the use of conventional method. The process independent variables were x_1 —reaction time (60 ± 30 min) and x_2 —the total concentration of salt amounted to 50 ± 10 wt%. Multiple dependent variables defining the physicochemical properties of prepared products were as follow: the content of Al^{3+} (y_1), Ca^{2+} (y_2), Mo^{6+} (y_3), NH_3 (y_4), P_2O_5 (y_5), specific surface area S_{BET} (y_6), oil absorption (y_7), and average particle size (y_8).

The aim of the experiments (performed according to established plan) was to determine the fractional design at 3 levels of the important factors affecting the investigated parameters and to find the right input values enabling to obtain a product with the expected properties [18]. A factorial plan and the results obtained from experiments are summarized in Table 1.

Sample preparation

Reagent grade substrates ($\geq 99\%$, POCH, Poland): $Al(NO_3)_3$, KOH, $(NH_4)_2HPO_4$, $CaCO_3$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, an aqueous ammonia (25 wt% of NH_3) and fresh $Al(OH)_3$ were used. Aluminium hydroxide was precipitated in the reaction of aluminium nitrate with potassium hydroxide at $pH = 7.5$ [19]. The molar ratio of Al^{3+} : Ca^{2+} : Mo^{6+} : PO_4^{3-} in the reaction mixture was 0.66:0.33:0.33:1 and the $pH = 6$ for the reaction medium at standards conditions. Suspension of aluminium hydroxide and calcium carbonate was dosed into the ammonium molybdate and ammonium phosphate solution at constant stirring velocity. The suspension of reactants with an appropriate pH was prepared in a glass reactor and treated for 30–90 min. The obtained precipitate was separated from the mother liquor using a vacuum filter, followed by triple washing with distilled water (weight ratio of liquid to the solid phase was 3:1). Finally, the obtained product was dried for 3 h at $70^\circ C$.

Anticorrosive properties of the modified aluminium phosphate for cold rolled steel were investigated by means of potentiodynamic polarization technique. For comparison two commercial anticorrosive pigments, i.e. aluminium dihydrogen tripolyphosphate (Rima-Cor ZFM, Gustav Grolman, Germany) and zinc phosphate (FC-M2, Złoty Stok, Poland) have been tested.

Sample characterization

The content of aluminium, calcium and molybdenum in the products was determined by ICP-AES technique (Optima 5300 DV, Perkin Elmer). The phosphates and ammonium content was determined by means of a spectrophotometric method [19] and ion selective electrode Orion 11–35 type, respectively [20]. The phase composition of the products was studied with X-ray diffraction analysis (CuK_α radiation, X'Pert PRO Philips diffractometer). The oil absorption (grams of oil required to form a homogeneous paste with 100 g of dry pigment) was determined according to PN-EN ISO 787-5 standard [21]. The measurements of Brunauer–Emmett–Teller surface area (S_{BET}) of materials were performed using Micrometrics Quadrasorb SI Quantachrome Instrument. N_2 adsorption/desorption measurements were carried out at liquid N_2 temperature. The average particle size of materials was determined by using a laser scanning microscope (VK-9700, Keyence, USA). The phosphates morphology was examined by scanning electron microscope SU-70 (Hitachi, Japan). Chemical composition of phosphates was determined using scanning electron microscope with a cold field emission (HITACHI SU8020, resolving power 1.3 nm), coupled with the energy dispersive X-ray analyzer (EDX—Thermo Scientific).

Tafel experiments in the range from -250 to 500 mV in relation to OCP (scan rate 0.25 mV s^{-1}) for an uncoated steel substrate (SEA 1008/1010, Q-Panels, Q-Lab Europe, England) were performed using DC105 software and FAS2 femtostat (Gamry, USA). As a

Table 1
Three-level $3^{(k-p)}$ fractional factorial design.

No. experiment (phosphate acronym)	Independent variables		Dependent variables							
	x_1	x_2	y_1 (wt%)	y_2 (wt%)	y_3 (wt%)	y_4 (wt%)	y_5 (wt%)	y_6 (m^2/g)	y_7 (g/100 g)	y_8 (nm)
1 (AP1)	30	40	16.31	17.61	1.28	0.19	7.10	8	36	247
2 (AP2)	30	50	16.33	17.12	0.75	0.32	6.97	10	42	230
3 (AP3)	30	60	14.41	14.57	3.04	1.30	14.5	26	54	221
4 (AP4)	60	40	15.49	16.55	0.96	0.16	12.7	10	48	260
5 (AP5)	60	50	14.43	18.54	5.28	1.04	13.3	20	55	233
6 (AP6)	60	60	14.23	16.18	1.09	0.42	20.1	21	61	252
7 (AP7)	90	40	15.09	16.72	0.59	0.09	13.4	6	39	270
8 (AP8)	90	50	13.12	13.86	1.32	1.05	17.6	63	71	229
9 (AP9)	90	60	10.52	10.59	5.12	4.91	23.4	15	48	319

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